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Wastewater treatment for dyes and heavy metals using modified pine sawdust as adsorbent

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Abstract

The main objective of this study was to evaluate the feasibility of removing hexavalent chromium and methylene blue, taken as representative species for heavy metals and dyes, respectively, from aqueous solutions, using industrial by-products, specifically pine sawdust, which comes ample in Greece and from many sources. The material was tested in raw form and after acid hydrolysis treatment under mild conditions. Adsorption experiments were carried out to investigate the effects of adsorbent dose, pH, contact time and initial adsorbent concentration, on the adsorption process. The adsorption kinetics and adsorption equilibrium were further studied using the data obtained from these experiments.

Keywords: Adsorption; methylene blue; chromium; sawdust; hydrolysis

1. Introduction

Dyes, pigments and heavy metals represent common and dangerous pollutants, released in large quantities from dye manufacturing, textile industry, as well as, pulp and paper processing, leather tanning, battery production, and other industries. Their removal has attracted much public and academic interest, owing to increased concern with their environmental impact. The conventional techniques used for dye and heavy metal removal are expensive, have moderate efficiencies and require sequential step

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Nomenclature

C	concentrations of Cr(VI) or MB in the bulk solution at time t in the case of batch adsorption process; also, the effluent concentration ($mg.L^{-1}$) in the case of the column adsorption process
C_0	initial Cr(VI) or MB concentration in the case of batch adsorption process ($mg.L^{-1}$)
C_e	equilibrium concentration of the adsorbate ($mg.L^{-1}$) for
k	first order rate constant for the batch adsorption process (min^{-1})
k_2	second order rate constant for the batch adsorption process (min^{-1})
K_F	Freundlich constant related to adsorption capacity (mg/g)(L/mg)1/n
K_L	Langmuir constant related to the energy of adsorption ($L.mg^{-1}$)
m	adsorbent mass (g)
n	inverse of the slope of the linearized (logarithmic) Freundlich isotherm, is related to adsorption intensity
NLRA	non-linear regression analysis
q	amount adsorbed per unit mass of the adsorbent for ($mg.g^{-1}$)
q_m	Langmuir constant related to the amount of Cr(VI) or MB adsorbed ($mg.g^{-1}$) when saturation is attained
q_t	amount of Cr(VI) or MB adsorbed per unit mass of the adsorbent ($mg.g^{-1}$) at time t
R	correlation coefficient
SEE	standard error of estimate
t	adsorption time (min).
V	volume of Cr(VI) or MB solution (L)

procedures [1, 2]. Other treatment processes suggested for their higher efficiencies, including reduction precipitation, ion exchange, electrochemical reduction, evaporation, reverse osmosis, and direct precipitation, necessitate a large exposed liquid surface area and long detention periods. Besides, most of these methods need high capital cost and recurring expenses such as chemicals, which are not suitable for small-to-medium sized industries [3].

Alternatively, adsorption methods have been widely proposed, on the premises of highly effective and economical process, provided that (i) the correct adsorbents are applied, and (ii) the environmental conditions favor adsorption. Activated carbon is the commonly adopted adsorbent for removing metals and dyes from wastewater, offering high efficiency at disproportionately high cost, prohibiting its broad applicability. Thus, the search for low-cost adsorbents, preferably derived from locally available waste materials, has become nowadays a main research focus. To date, numerous studies on the use of low-cost materials have been published. The various materials tested include raw rice bran [4], ethylenediamine-modified rice hull [5], hazelnut shell [6], pine needles, olive cake, wool, almond, soya cake [7], maple saw dust [8], saw dust activated carbon [9] and sugarcane bagasse [10], to mention but a few. The use of such

materials has double benefits to the environment: these materials are converted into high added value adsorbents, whereas these adsorbents are suitable for water and wastewater purification.

This work evaluates the feasibility of removing hexavalent chromium, Cr(VI) and Methylene Blue, MB, from aqueous solutions, using pine sawdust, an industrial by-product, which comes ample in Greece and from many sources. The sawdust was tested untreated and after acid hydrolysis treatment under mild conditions (100 ^{o}C) to reduce costs. Batch adsorption experiments were carried out to investigate the effects of adsorbent dose, solution pH, contact time and initial adsorbent concentration, on the adsorption process. The adsorption kinetics and isotherms were studied using the experimental data obtained from these experiments.

2. Materials and methods

2.1. Material Development

The Scots Pine (*Pinus Sylvestris L.*) sawdust used was obtained from a local furniture manufacturing company, as a suitable source for full-scale/industrial applications. The moisture content of the material when received was 8.7% w/w; after screening, the fraction with particle sizes between 0.2 and 1 mm was isolated. The composition of the raw material was as follows (expressed in % w/w on a dry weight basis): 40.1% cellulose measured as glucan; 28.5% hemicelluloses (16.0% measured as manan, 8.9% measured as xylan and the rest 3.6% measured as arabinan); 27.7% Klason acid-insoluble lignin, 0.2% ash, and 3.5% extractives and other acid soluble components (e.g. acid soluble lignin). The acid pretreatment process was performed in a 500-mL glass batch reactor, equipped with an internal thermocouple, immersed in a heating oil bath. The acid treatment time was 0.5 - 5 h; 0.11 – 3.6 N sulfuric acid solutions catalyzed the reaction at a liquid-to-sawdust ratio of 10:1 (liquid phase 400 mL, solid material 40 g). The reaction ending temperature was 100^{o}C.

2.2. Adsorption Isotherm Studies

Adsorption isotherms were derived from batch experiments. Following the batch procedure, accurately weighed quantities of adsorbent were transferred into 0.8-L bottles, where 0.5 L of adsorbate solution were added. The initial concentration varied from 15 mg/L to 75 mg/L for hexavalent chromium, Cr(VI), and 1.6 to 156 mg/L mg/L for Methylene Blue, MB, the sorbent weight was 2 g (i.e. m/V=4 g/L) for Cr(VI) and 0.5 g (i.e. m/V=1 g/L) for MB, pH equals 2.0 for Cr(VI) and 8.0 for MB the temperature was 23 ^{o}C. The bottles were sealed and mechanically tumbled for a period of 7 days. This time period was chosen after experimental studies (the time varied from 4 h to 14 days), to ensure that nearly equilibrium conditions were achieved. The resulting solution concentrations were determined and the equilibrium data from each bottle represented one point on the adsorption isotherm plots.

2.3. Kinetic studies

Adsorption rate batch experiments were conducted in a 2-L completely mixed glass reactor fitted with a twisted blade-type stirrer, operating at 100-600 rpm for keeping the lignocellulosic material in suspension. The reactor, containing 1 L aquatic Cr(VI) or MB solution, was placed into a water bath to keep temperature constant at the desired level (23 ^{o}C). The sorbent weight varied from 1 g to 8 g (i.e. m/V=1-8 g/L) for Cr(VI) and the adsorbent dose for MB was 1 g. The initial concentration varied from 1.6 mg/L to 7.7 mg/L for Cr(VI) and 1.6 mg/L to 156 mg/L for MB. The effect of contact time, adsorbent

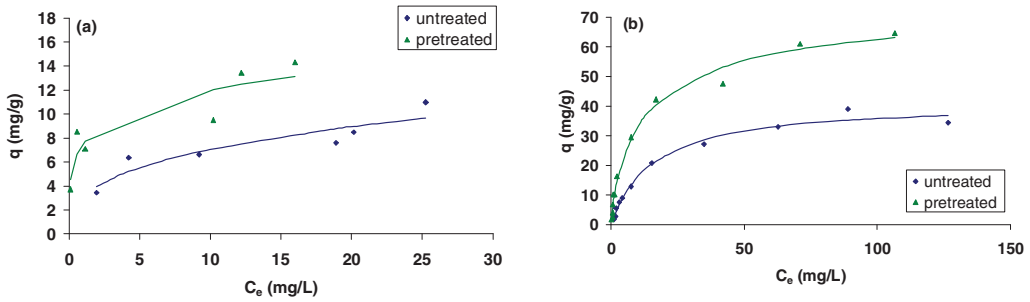

Fig. 1. The adsorption isotherms of (a) Cr(VI) and (b) MB adsorption on untreated and hydrolyzed (at 100°C with 3.6 N H_2SO_4 for 2h) pine sawdust. The theoretical curves are according to the Sips model.

dose and initial concentrations of adsorbate on the uptake of Cr(VI) and MB were studied in batch experiments. The pH effect was also studied in the range of 1.2-3.4 (the pH of the solutions was adjusted using dilute H_2SO_4) for Cr(VI) and in the range of 1.5 to 13 (the initial pH of the dye solutions was adjusted using dilute H_2SO_4 or NaOH solutions, as appropriate) for MB.

2.4. Analytical techniques

The Saeman *et al.* [11] technique was used for the quantitative saccharification of the untreated lignocellulosic material and the acid hydrolysis reaction solid residues. The filtrates from the quantitative saccharification were analyzed for glucose, xylose, manose and arabinose using high-performance liquid chromatography (HPLC, Agilent 1200) with Aminex HPX-87H Column, refractive index detector and 5 mM H_2SO_4 in water as the mobile phase. Cellulose was estimated as glucan and hemicelluloses were estimated as xylan, manan and arabinan. Finally, the acid-insoluble lignin (Klason lignin) was determined according to the Tappi T222 om-88 method [12]. The concentration of Cr(VI) in the solution was measured by using a HACH DR4000U UV–visible spectrophotometer, according the Method 8023 (1,5-Diphenylcarbohydrazide Method) HACH DR/4000 PROCEDURE, CHROMIUM, HEXAVALENT. The concentration of methylene blue in the solution was obtained by measuring O.D. at 663 nm respectively, using the same spectrophotometer. Finally, pH measurements were made using a digital pH meter (MultiLab model 540).

3. Results and Discussion

3.1. Adsorption isotherms

The adsorption isotherms of Cr(VI) and MB for untreated and acid-hydrolyzed pine sawdust were studied. An example for untreated and acid-hydrolyzed pine sawdust at 100°C with 3.6 N H_2SO_4 for 2h is presented in Fig. 1. Furthermore, the simulation of these experimental data and the estimation of the untreated and pretreated sawdust adsorption capacity was based on the Freundlich [13] Langmuir [14] and Sips [15] isotherm models. These three models were commonly used for investigating the adsorption

of a variety of dyes, heavy metals on various lignocellulosic materials and activated carbons. The Freundlich [13] isotherm is given by the following equation:

$$q = K_F \cdot (C_e)^{1/n} \quad (1)$$

where q is the amount adsorbed per unit mass of the adsorbent (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L) and K_F, n are the Freundlich constants related to adsorption capacity and intensity, respectively. Deriving the logarithmic form of eq. (1):

$$\log q = \log K_F + \frac{1}{n} \log C_e \quad (2)$$

The Freundlich constants K_F and n were estimated by linear and non-linear regression analysis (NLRA) from the experimental adsorption data obtained at 23^0C for Cr(VI) and MB . The theoretical curves were estimated according to the Freundlich equation. Cr(VI) and MB adsorption isotherm-parameters K_F and n for linear regression analysis for original and acid-treated pine sawdust are presented in Fig. 2. The correlation coefficients, R, were very satisfactory (see Table 1). In Fig. 3, Cr(VI) and MB adsorption isotherm-parameters K_F and n using NLRA are presented. The standard error estimate (SEE) were calculated in each case by the following expression

$$SEE = [\sum_{i=1}^{n'} (y_i - y_{i,theor})^2 / (n' - p')]^{1/2} \quad (3)$$

where: y_i is the experimental value of the depended variable, $y_{i,theor}$ is the theoretical or estimated value of the depended variable, n' is the number of the experimental measurements and p' is the number of parameters (the difference $n - p'$ being the number of the degrees of freedom). The fitting of the Freundlich adsorption model to the experimental data was very satisfactory (see Table 2). The hydrolysis treatment was using 0.11-3.6N H_2SO_4 for 2 h (see Fig. 2 a, b and 3 a, b), not including preheating time. The K_F values estimated for the acid-treated samples were significantly higher than those of the untreated material, indicating an increased adsorption capacity of the former. The Freundlich parameter n was also affected by the acid-treatment conditions.

The Langmuir isotherm equation [14] is based on the following 'pseudo-monolayer' adsorption model.

$$q = K_L q_m C_e / (1 + K_L C_e) \text{ or } 1/q = 1/q_m + 1/(K_L q_m C_e) \quad (4)$$

where K_L is the Langmuir constant related to the energy of adsorption (L.mg^{-1}) and q_m the amount of dyes and heavy metals adsorbed (mg.g^{-1}) when saturation is attained. In cases where the isotherm experimental data approximates the Langmuir equation, the parameters K_L and q_m can be obtained by plotting $1/q$ versus $1/C_e$ or by NLRA which is preferable. The Langmuir's isotherm curve of Cr(VI) and MB adsorption on original pine sawdust and on pine sawdust pretreated with 0.1125-3.6 N H_2SO_4 and pretreatment time for 2 h (not including preheating time). All these are presented in Fig. 4 (a, b) and Table 3 for linear regression analysis and in Fig. 5 and Table 4b(a, b) for NLRA.

The Sips (Langmuir – Freundlich) [15] isotherm equation is.

$$q = [q_m \cdot (K_L \cdot C_e)^{1/n}] / [1 + (K_L \cdot C_e)^{1/n}] \quad (5)$$

Table 1. The Freundlich parameter values, estimated by linear regression analysis, as affected by the hydrolysis catalyst concentration (0.11-3.6 N H_2SO_4) and hydrolysis time (0.5 - 5 h).

		Chromiun (VI)			Methylene Blue		
H_2SO_4 (N)	t (h)	K_F	n	R	K_F	n	R
0	0	3.05	2.79	0.9320	2.62	1.59	0.9622
0.11	0.5	4.17	4.27	0.9423	3.28	1.75	0.9700
0.23	0.5	5.02	3.80	0.9883	3.78	1.80	0.9640
0.45	0.5	7.54	5.70	0.9657	4.54	1.87	0.9816
1.8	0.5	7.31	6.35	0.9604	4.28	1.65	0.9632
3.6	0.5	4.18	3.56	0.9209	5.73	2.27	0.9609
0.23	2	3.16	2.49	0.9827	4.24	1.97	0.9592
0.45	2	5.55	4.46	0.9722	5.12	2.39	0.9824
0.9	2	4.12	2.91	0.9845	4.50	2.02	0.9631
1.8	2	8.46	5.82	0.9911	6.23	2.37	0.9692
3.6	2	7.28	4.61	0.9244	5.49	2.03	0.9622
0.45	3	3.25	2.87	0.9742	4.64	1.88	0.9344
0.9	3	3.19	2.52	0.9209	6.53	2.35	0.9382
1.8	3	4.60	4.35	0.9665	5.38	2.03	0.9542
0.23	4	2.44	2.04	0.8255	4.91	2.57	0.9356
0.45	4	4.57	2.90	0.9825	5.68	2.21	0.9847
0.9	4	1.54	1.75	0.8360	4.76	1.89	0.9760
1.8	4	4.48	3.42	0.8017	5.84	2.15	0.9817
3.6	4	7.04	6.70	0.9439	6.64	1.78	0.9489
0.11	5	4.84	3.21	0.9933	4.80	2.31	0.9421
0.23	5	7.87	4.91	0.9739	3.86	1.83	0.9730
1.8	5	7.04	3.49	0.9647	4.92	1.93	0.9778

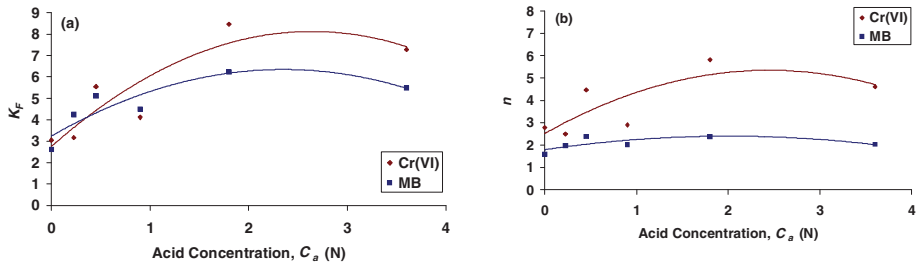

Fig. 2. The Freundlich isotherm (a) capacity coefficient K_F and (b) intensity coefficient n of Cr(VI) and MB adsorption on pretreated pine sawdust vs H_2SO_4 concentration, estimated using linear regression analysis . Adsorption: 23°C, initial concentration C_0=15-75 mg/L for Cr(VI) and 1.6-156 mg/L for MB, m/V=4 g/L for Cr(VI) and 1 g/L for MB, pH=2.0 for Cr(VI) and 8.0 for MB. Acid hydrolysis: 100°C, 2 h, 0.11-3.6 N H_2SO_4, solid : liquid ratio 1:10.

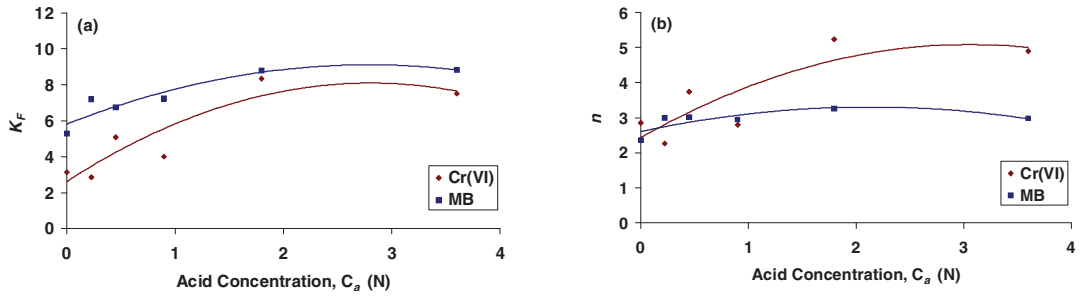

Fig. 3. The Freundlich isotherm (a) capacity coefficient K_F and (b) intensity coefficient n of Cr(VI) and MB adsorption on pretreated pine sawdust vs H_2SO_4 concentration, estimated using NLRA . Adsorption: 23°C, initial concentration C_0=15-75 mg/L for Cr(VI) and 1.6-156 mg/L for MB, m/V=4 g/L for Cr(VI) and 1 g/L for MB, pH=2.0 for Cr(VI) and 8.0 for MB. Acid hydrolysis: 100°C, 2 h, 0.11-3.6 N H_2SO_4, solid : liquid ratio 1:10.

Table 2. The Freundlich parameter values, estimated by NLRA, as affected by the hydrolysis catalyst concentration (0.11-3.6 N H_2SO_4) and hydrolysis time (0.5 - 5 h).

		Chromiun (VI)			Methylene Blue		
H_2SO_4 (N)	t (h)	K_F	n	SEE	K_F	n	SEE
0	0	3.13	2.85	1.11	5.27	2.36	3.67
0.11	0.5	4.02	3.97	1.00	5.92	2.55	3.70
0.23	0.5	4.60	3.29	0.63	6.49	2.51	4.02
0.45	0.5	7.59	5.69	1.34	6.53	2.40	2.38
1.8	0.5	6.69	4.68	1.13	7.54	2.34	3.69
3.6	0.5	3.48	2.81	1.75	8.95	3.38	4.72
0.23	2	2.86	2.26	0.71	7.19	2.99	4.21
0.45	2	5.07	3.74	0.86	6.74	3.01	2.59
0.9	2	4.01	2.80	0.74	7.22	2.94	3.43
1.8	2	8.33	5.23	0.67	8.80	3.26	3.67
3.6	2	7.50	4.90	1.83	8.83	2.98	4.11
0.45	3	3.05	2.67	0.91	8.58	3.03	5.94
0.9	3	3.04	2.38	1.39	10.36	3.71	6.15
1.8	3	4.65	4.42	0.44	6.62	2.37	2.33
0.23	4	3.04	2.43	1.60	7.34	3.83	4.72
0.45	4	4.72	3.03	0.69	7.24	2.71	1.59
0.9	4	1.84	1.93	1.42	6.91	2.39	4.30
1.8	4	4.95	3.95	1.55	7.88	2.70	2.89
3.6	4	6.75	5.60	1.69	10.96	2.53	4.80
0.11	5	4.75	3.12	0.50	7.94	3.64	4.78
0.23	5	7.16	3.60	1.19	5.02	2.16	4.57
1.8	5	7.16	3.60	1.52	7.44	2.61	2.94

Table 3. The Langmuir parameter values, estimated by linear regression analysis as affected by the hydrolysis catalyst concentration (0.11-3.6 N H_2SO_4) and hydrolysis time (0.5 - 5 h).

		Chromiun (VI)			Methylene Blue		
H_2SO_4 (N)	t (h)	K_F	n	R	K_F	n	R
0	0	10.47	0.26	0.9675	24.05	0.11	0.9709
0.11	0.5	7.94	1.49	0.9060	26.55	0.14	0.9750
0.23	0.5	9.31	2.49	0.9453	24.09	0.19	0.9711
0.45	0.5	9.93	27.53	0.9527	24.24	0.28	0.9935
1.8	0.5	9.34	70.78	0.9250	24.86	0.33	0.9886
3.6	0.5	8.38	1.55	0.9254	25.47	0.38	0.9959
0.23	2	10.67	0.39	0.9559	33.09	0.16	0.9901
0.45	2	9.33	5.12	0.9410	13.84	1.19	0.9675
0.9	2	10.96	0.59	0.9700	34.52	0.18	0.9706
1.8	2	9.88	3.20	0.9355	25.67	0.47	0.9934
3.6	2	10.91	5.81	0.9577	48.69	0.16	0.9751
0.45	3	9.29	0.52	0.9684	52.42	0.09	0.9756
0.9	3	11.97	0.25	0.9387	36.45	0.30	0.9965
1.8	3	10.96	0.28	0.9745	107.73	0.05	0.9209
0.23	4	22.35	0.06	0.8057	20.83	0.37	0.9966
0.45	4	11.82	0.67	0.9904	20.53	0.64	0.9933
0.9	4	17.82	0.05	0.7513	35.58	0.17	0.9865
1.8	4	13.13	0.29	0.8410	32.83	0.95	0.9605
3.6	4	9.15	0.10	0.9337	30.09	0.31	0.9200
0.11	5	10.17	1.32	0.9722	22.07	0.30	0.9895
0.23	5	10.02	34.94	0.9368	34.01	0.12	0.9901
1.8	5	10.75	5.43	0.9170	30.53	0.22	0.9981

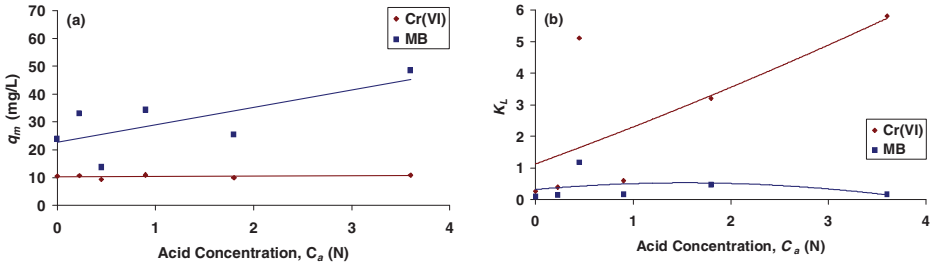

Fig. 4. The Langmuir isotherm (a) amount of dyes or heavy metals adsorbed q_m and (b) constant related to the energy of adsorption K_L of Cr(VI) and MB adsorption on pretreated pine sawdust vs. H_2SO_4 concentration, estimated using linear regression analysis . Adsorption: 23ºC, initial concentration C_0=15-75 mg/L for Cr(VI) and 1.6-156 mg/L for MB, m/V=4 g/L for Cr(VI) and 1 g/L for MB, pH=2.0 for Cr(VI) and 8.0 for MB. Acid hydrolysis: 100ºC, 2 h, 0.11-3.6 N H_2SO_4, solid : liquid ratio 1:10.

Table 4. The Langmuir parameter values, estimated by NLRA, as affected by the hydrolysis catalyst concentration (0.11-3.6 N H_2SO_4) and hydrolysis time (0.5 - 5 h).

		Chromiun (VI)			Methylene Blue		
H_2SO_4 (N)	t (h)	q_m	K_L	*SEE*	q_m	K_L	*SEE*
0	0	10.68	0.25	1.24	41.60	0.06	1.68
0.11	0.5	8.71	0.81	1.42	38.18	0.08	1.30
0.23	0.5	12.95	0.30	1.63	44.79	0.07	2.74
0.45	0.5	14.76	0.46	2.53	45.65	0.08	2.85
1.8	0.5	13.80	0.47	2.23	55.23	0.08	2.60
3.6	0.5	11.44	0.29	2.27	34.24	0.20	1.82
0.23	2	15.78	0.11	1.16	33.38	0.14	1.96
0.45	2	11.86	0.46	1.85	31.66	0.12	2.81
0.9	2	13.05	0.30	1.25	34.34	0.13	1.25
1.8	2	14.39	0.92	2.70	34.86	0.19	1.82
3.6	2	12.43	2.86	2.29	40.64	0.15	2.18
0.45	3	9.93	0.46	1.50	38.21	0.17	3.50
0.9	3	12.76	0.21	1.74	34.65	0.26	3.87
1.8	3	11.04	0.27	0.41	51.03	0.05	5.08
0.23	4	13.96	0.15	1.53	23.96	0.25	3.55
0.45	4	13.00	0.46	1.16	38.85	0.11	2.99
0.9	4	15.29	0.07	1.53	45.05	0.09	2.37
1.8	4	11.23	0.52	1.46	43.41	0.10	1.81
3.6	4	11.29	1.26	2.81	65.72	0.11	3.27
0.11	5	12.85	0.43	1.40	28.69	0.19	2.29
0.23	5	15.75	0.60	2.21	47.99	0.05	5.98
1.8	5	20.30	0.27	2.05	43.98	0.09	1.68

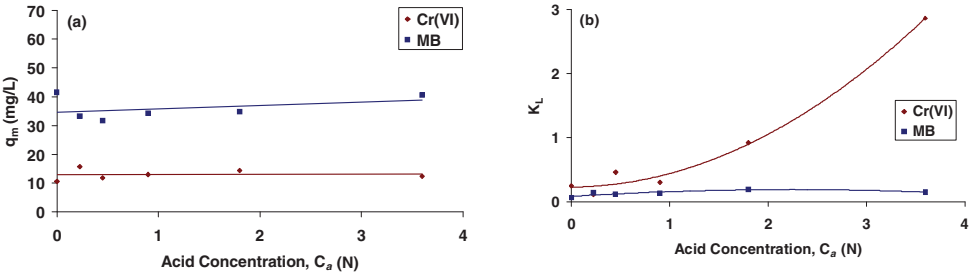

Fig. 5. The Langmuir isotherm (a) amount of dyes or heavy metals adsorbed q_m and (b) constant related to the energy of adsorption K_L of Cr(VI) and MB adsorption on pretreated pine sawdust vs. H_2SO_4 concentration, estimated using NLRA . Adsorption: 23°C, initial concentration C_0=15-75 mg/L for Cr(VI) and 1.6-156 mg/L for MB, m/V=4 g/L for Cr(VI) and 1 g/L for MB, pH=2.0 for Cr(VI) and 8.0 for MB. Acid hydrolysis: 100°C, 2 h, 0.11-3.6 N H_2SO_4, solid : liquid ratio 1:10.

Table 5. The Sips parameter values, estimated by NLRA, as affected by the hydrolysis catalyst concentration (0.11-3.6 N H_2SO_4) and hydrolysis time (0.5 - 5 h).

		Chromium (VI)				Methylene Blue			
H_2SO_4 (N)	t (h)	q_m	K_L	n	SEE	q_m	K_L	n	SEE
0	0	77.28	0.0002465	2.61	1.28	41.17	0.064435	0.98	1.77
0.11	0.5	56.15	0.0001165	3.53	1.16	36.48	0.092261	0.90	1.30
0.23	0.5	144.47	0.0000233	3.12	0.76	48.98	0.055046	1.16	2.79
0.45	0.5	39.78	0.0016266	4.49	1.54	78.04	0.014044	1.64	2.08
1.8	0.5	108.98	0.0000071	4.35	1.36	44.16	0.133456	0.89	4.68
3.6	0.5	220.27	0.0000156	2.69	2.03	33.27	0.212827	0.88	1.84
0.23	2	172.57	0.0001431	2.16	0.83	31.59	0.162516	0.81	1.93
0.45	2	105.60	0.0000251	3.57	1.03	46.68	0.030116	1.73	2.12
0.9	2	125.29	0.0001263	2.63	0.86	34.91	0.124665	1.05	1.31
1.8	2	90.08	0.0000185	4.79	0.83	36.64	0.162786	1.17	1.80
3.6	2	73.24	0.0000883	4.32	2.12	42.40	0.130074	1.12	2.24
0.45	3	146.18	0.0000544	2.54	1.07	35.13	0.216630	0.67	3.26
0.9	3	191.85	0.0000730	2.31	1.61	35.23	0.246965	1.07	4.07
1.8	3	11.77	0.2495535	1.22	0.41	579.81	0.000032	2.31	2.65
0.23	4	162.57	0.0000967	2.33	1.84	24.06	0.243344	1.02	3.75
0.45	4	118.22	0.0001257	2.82	0.80	92.37	0.005124	2.06	1.43
0.9	4	162.54	0.0002316	1.87	1.67	47.13	0.081791	1.10	2.47
1.8	4	9.77	0.5150766	0.24	1.25	50.63	0.061083	1.31	1.53
3.6	4	76.57	0.0000057	5.21	1.99	77.19	0.066450	1.30	2.80
0.11	5	141.84	0.0000506	2.94	0.60	27.21	0.215168	0.74	2.15
0.23	5	191.60	0.0000116	3.51	1.42	730.72	0.000029	2.09	4.85
1.8	5	341.14	0.0000394	2.53	1.30	51.39	0.057957	1.29	1.24

where K_L and q_m is the Langmuir constants, and n the Freundlich constant. The parameters K_L, q_m and n can be obtained by NLRA. In Table 5 the estimated parameter values for the experimental data obtained in the present study are presented. The adsorption curves of Cr(VI) and MB for untreated and acid-hydrolyzed pine sawdust in Fig. 1 were estimated according to the Sips model.

3.2. Kinetics

The kinetics of adsorption of Cr(VI) and MB on various materials has been extensively studied using various kinetic equations. The widely used Lagergren equation [16] is shown below:

$$q - q_t = q \cdot e^{-k \cdot t} \tag{6}$$

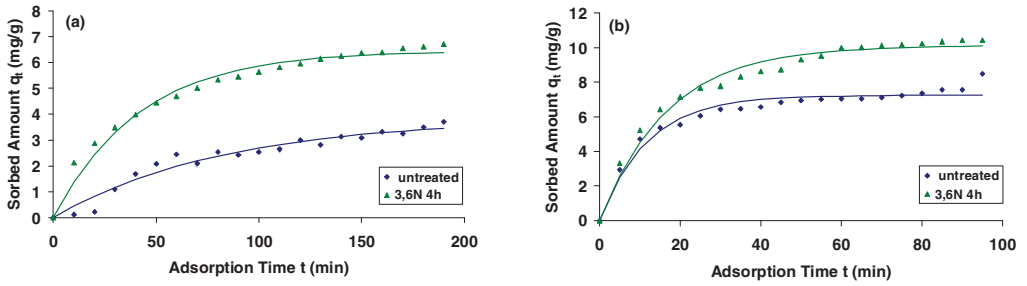

Fig. 6. The Lagergren kinetics of (a) Cr(VI) and (b) MB adsorption on untreated and acid-hydrolyzed pine sawdust at 100°C with 3.6 N H_2SO_4 for 4h. Adsorption: 23°C, initial concentration C_0=7 mg/L for Cr(VI) and 12 mg/L for MB, m/V=4 g/L for Cr(VI) and 1 g/L for MB, pH=2.0 for Cr(VI) and 8.0 for MB, solid : liquid ratio 1:10.

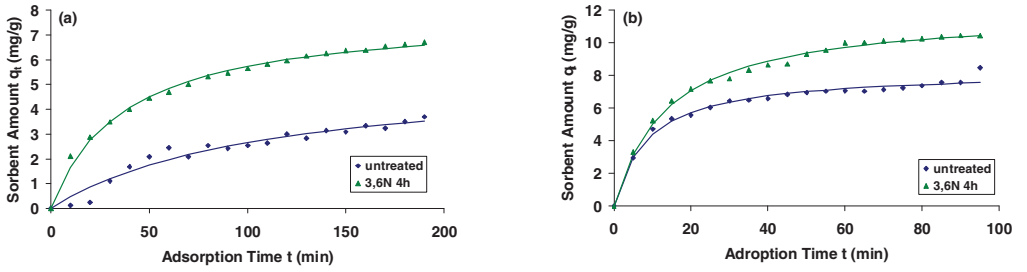

Fig. 7. The second order kinetics of (a) Cr(VI) and (b) MB adsorption on untreated and acid-hydrolyzed pine sawdust at 100°C with 3.6 N H_2SO_4 for 4h. Adsorption: 23°C, initial concentration C_0=7 mg/L for Cr(VI) and 12 mg/L for MB, m/V=4 g/L for Cr(VI) and 1 g/L for MB, pH=2.0 for Cr(VI) and 8.0 for MB, solid : liquid ratio 1:10.

where q and q_t are the amounts of Cr(VI) or MB adsorbed per unit mass of the adsorbent (in mg/g) at equilibrium time and adsorption time t, respectively, while k is the pseudo-first order rate constant for the adsorption process (in min^{-1}). Moreover, $q = (C_o - C_e)V/m$ and $qt = (C_o - C)V/m$, where C, C_0 , C_e are the concentrations of Cr(VI) or MB in the bulk solution at time t, 0, and infinite, respectively, while m is the weight of the adsorbent used (in g), and V is the solution volume (in mL). Further modification of eq. (6) in logarithmic form gives:

$$\ln(q - q_t) = \ln q - k \cdot t \qquad (7)$$

The plots of $\ln(q - q_t)$ vs. t for all Cr(VI) or MB adsorbent systems were found to be linear, indicating the possibility of first order nature of the adsorption process. The Cr(VI) or MB adsorption kinetics by untreated and pretreated (acid hydrolysis with 0.11-3.6 N sulfuric acid at 100°C for 0.5-5 h + preheating period 40 min) pine sawdust were studied. An example (acid hydrolyzed sawdust with 3.6 N sulfuric acid

at 100°C for 4 h) is presented in Fig. 6. In the case of the untreated and the pretreated sawdust, the estimated by NLRA values of the first order rate constants k and the *SEE*-values were determined. All *SEE*-values were found low, indicating the high applicability of this kinetic equation to the adsorption of Cr(VI) and MB on pine sawdust.

Moreover, the commonly used [17, 18] second order kinetic model is

$$q_t = q - \left[q^{-1} + k_2 t\right]^{-1} \quad (8)$$

The second order kinetics are presented in Fig. 7 for Cr(VI) and MB for untreated and pretreated pine sawdust. The NLRA-estimated values of the second order rate constants k_2 and the *SEE*-values were determined. All *SEE*-values were found to be a little lower than those of the first-order kinetic model, indicating the marginally higher applicability of the second-order kinetic equation to the adsorption of Cr(VI) and MB on pine sawdust.

4. Conclusions

According to the above results, acid-treatment of the pine sawdust enhances considerably the materials adsorption properties as regards metals and dyes cleaning from aquatic environment. Thus, this low-cost widely available material could be used as an alternative adsorbent to commercial activated carbons. Furthermore, considering that sawdust is an industrial waste, acid hydrolyzed lignocellulosic materials are industrial wastes from the bio-ethanol production industry, and sulfuric acid can be recovered as a spent liquid from various chemical operations, this process of modified adsorbent production might be considered to take place within an 'Industrial Ecology' framework.

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